Further Studies of the Core Binding Energy–Proton Affinity Correlation in Molecules

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Abstract: Core-level binding-energy shifts were measured for O1s levels in alcohols, ethers, acids, aldehydes, esters, and acetone, N1s levels in ammonia and aliphatic amines, P2p levels in phosphine and its methyl derivatives, and S2p levels in H_2S and its methyl derivatives. A total of 46 compounds were studied. The core-level shifts correlated well with gas-phase proton affinities, thereby extending and supporting earlier results of Martin and Shirley, Davis and Rabalais, and Carroll, Smith, and Thomas. In the amines, for which the data are most precise, a good correlation was observed for all 16 molecules taken together. On a finer scale, each series of amines (primary, secondary, tertiary) showed a linear correlation, while ammonia and its methyl derivatives showed a linear correlation with different slopes. These two correlations are interpreted as responses of the system to long-range effects and to changes in the local bonds, respectively. Similar behavior was observed in the single-bonded oxygen compounds. Excellent linear correlations were observed in the compounds of the third period elements phosphorus and sulfur. Differences in the slopes were tentatively attributed to changes in nuclear position on protonation. Analysis of the oxygen data supports the conclusion of Carroll et al. that protonation of carboxyl groups occurs on the keto oxygen. These results suggest that core-level shifts can be used to predict proton affinities.

I. Introduction

Chemists have devoted considerable effort to understanding the fundamental chemical concept of basicity. In a widely accepted early definition, Bronsted[1] described basicity as the tendency of a molecule B to accept a proton in the reaction

$$B + H^+ \rightarrow BH^+ \qquad -PA \qquad (1)$$

The enthalpy change of this reaction is $-PA$, where PA is the proton affinity of B. This concept of basicity was generalized further, and freed from reference to a specific acid (H^+) by Lewis, who defined a base as a molecule that tends to donate a valence electron "lone pair" in bonding with a Lewis acid; i.e., a molecule that can accept an electron pair.[2] Thus B in eq 1 is also a Lewis base because it contributes a lone pair in forming the B–H^+ bond.

Problems are encountered when attempting to relate these concepts to microscopic properties of isolated molecules. Measurements that yield basicity information are hard to make, and few are available. Gas-phase basicities can follow trends opposite to those observed in solution,[3] showing that the solution results may be dominated by solvation effects. It is of considerable importance to be able to separate the local molecular effects from those of solvation, because of the bearing of these two effects on the more general question of solution vs. gas-phase chemical reactivity. Recently Martin and Shirley,[4] and independently Davis and Rabalais,[5] have shown the relationship between trends in basicity and core-level binding energies. They further showed that the trends in general resulted from the interplay of initial-state (inductive) effects and final-state (polarization) effects, with the latter dominating for the proton affinities and O1s binding energies (E_B(O1s)) of a series of aliphatic alcohols. This can be understood on the basis that the OH group has essentially the same local charge distribution and electrostatic potential in different alcohols ROH. Introduction of a positive "test charge", either by adding a proton to form ROH_2^+ or by removing an O1s electron to form a positive 1s hole, is accompanied by a reaction energy that varies with R mainly through the variation of the R group's ability to stabilize the positive charge through polarization. The relation of the O1s binding-energy trends with Lewis basicity is obvious, while its relation with Bronsted basicity is nearly quantitative for the few cores studied in ref 4 and 5.

Carroll, Smith, and Thomas[6] added more single- and double-bonded oxygen compounds and some di- and triatomic molecules to the correlation between E_B(O1s) and $-PA$, and they discussed the position of protonation for some cases. In this paper we report additional O1s and N1s core-level binding energies, and correlations with PA values in series of alcohols, ethers, acids, esters, aldehydes, acetone, and aliphatic amines. The correlation has been extended to the third row by measurements of core-level binding-energy shifts in phosphine and methyl-substituted phosphines, as well as the series H_2S, CH_3SH, $(CH_3)_2S$. Experimental procedures are described in section II, and results are given in section III. The results are discussed in the above order in section IV.

II. Experimental Section

All of the compounds were obtained commercially except for $P(CH_3)H_2$, which was made by the method given by Jolly.[7] The methyl-substituted phosphines were purified on a vacuum line, and their purities were checked by vapor-pressure measurements. Gaseous N_2, O_2, and PF_3, which were used as binding-energy standards, were run along with the appropriate compounds. The sulfur compounds were run with Ne as a standard. The spectra were taken on the 50-cm radius Berkeley magnetic spectrometer using Mg $K\alpha_{1,2}$ radiation. They were fitted to Gaussian peaks using a nonlinear least-squares computer program. In the case of O_2, the two lines were fixed at an area ratio of 1 to 2 and a separation of 1.12 eV. For the acids and esters the peaks from the two oxygens were constrained to have the same area.

III. Results

The binding-energy shifts are shown in Table I along with the proton affinities for the various molecules studied. In some cases there was more than one literature value of the PA. In cases for which there was no clear reason to choose among various proton affinity values, preference was given to data in which an entire series was measured at the same laboratory. The worst disagreement is for acetone, in which the PA values are separated by 14 kcal while the stated errors are 2 kcal.[8,9]

The errors in the relative core binding energies are smaller than the PA errors in the oxygen compounds, amounting to 0.02–0.05 eV (0.5–1.2 kcal), being largest for molecules containing two oxygens where there is a problem of resolv-

Table I. Binding Energy Shift from Reference Molecule, Proton Affinity, and Shifts Relative to the Basic Hydride

Molecule	$-E_B$ shift		PA used	Other PA measurements	$-\Delta E_B$	ΔPA
Water	3.43 (2)		165 (3)[a]	165 (3),[b] 164 (4)[c]	0.00	0 (3)
Methanol	4.22 (2)		180 (3)[d]	182 (3)[b]	0.79	15 (3)
Ethanol	4.53 (2)		187 (2)[a]	186[d]	1.10	22 (2)
Propanol	4.60 (2)		189 (2)[a]		1.17	24 (2)
2-Propanol	4.75 (2)		193 (5)[a]	193 (5),[e] 195[f]	1.32	28 (5)
tert-Butyl alcohol	4.96 (2)		198 (3)[a]	206[f]	1.53	33 (3)
Dimethyl ether	4.74 (2)		187 (1)[d]	190 (5),[a] 186,[d] 186[e]	1.31	22 (1)
Diethyl ether	5.24 (2)		199[b]	205 (3)[a]	1.81	34
Formaldehyde	3.77 (2)		168 (1)[g]	166,[d] 165 (3)[c]	0.34	3 (1)
Acetaldehyde	4.71 (2)		185 (2)[g]	183 (2),[e] 183[d]	1.28	20 (2)
Propionaldehyde	4.85 (2)		187 (2)[g]	187[d]	1.42	22 (2)
Acetone	5.37 (2)		202 (2)[a]	188 (2),[b] 196 (2),[h] 202[i]	1.94	37 (2)
Formic acid	2.65 (3)	4.35 (3)	175 (5)[a]	179 (3),[b] 166[j]	0.92	10 (5)
Acetic acid	3.20 (3)	4.99 (3)	188 (3)[a]	184 (3)[j]	1.56	23 (3)
Propionic acid	3.31 (3)	5.07 (3)	~190[a]	185 (3)[j]	1.64	~25
Trifluoroacetic acid	2.00 (3)	3.75 (3)	167 (3)[a]		0.32	2 (3)
Methyl formate	3.46 (5)	4.86 (5)	188 (3)[a]		1.43	23 (3)
Ethyl formate	3.72 (5)	5.01 (5)	198 (3)[a]		1.58	33 (3)
Propyl formate	3.80 (5)	5.08 (5)	198 (3)[a]		1.65	33 (3)
Methyl acetate	3.86 (5)	5.39 (5)	202 (2)[a]		1.96	37 (2)
Ethyl acetate	4.07 (5)	5.49 (5)	205 (3)[a]		2.06	40 (3)
Propyl acetate	4.13 (5)	5.55 (5)	207 (3)[a]		2.12	42 (3)
Methyl propionate	4.03 (5)	5.58 (5)	205 (3)[a]		2.15	40 (3)
Ammonia	4.41 (2)		207 (3)[k,l]		0.00	0 (3)
Methylamine	4.76 (2)		218.4[l]	211 (3),[b] 216.3 (6)[m]	0.35	11.4
Ethylamine	4.95 (2)		221.1 (2)[l]	218.8 (6)[m]	0.54	14.1 (2)
n-Propylamine	5.03 (2)		222.3 (2)[l]		0.62	15.3 (2)
n-Butylamine	5.05 (2)		222.8 (2)[l]		0.64	15.8 (2)
Isopropylamine	5.11 (2)		223.3 (2)[l]	221.2 (6)[m]	0.70	16.3 (2)
sec-Butylamine	5.19 (2)		224.4 (2)[l]		0.78	17.4 (2)
tert-Butylamine	5.24 (2)		225.4 (2)[l]	223.3 (6)[m]	0.83	18.4 (2)
Dimethylamine	5.00 (2)		224.9 (2)[l]	222.4 (6)[m]	0.59	17.9
Diethylamine	5.36 (2)		230.1 (2)[l]		0.45	23.1
Di-*n*-propylamine	5.46 (2)		231.9 (2)[l]		1.05	24.9
Di-*n*-butylamine	5.50 (2)		232.7 (2)[l]		1.09	25.7
Diisopropylamine	5.62 (2)		234.3 (2)[l]		1.21	27.3
Trimethylamine	5.11 (2)		229.1 (2)[l]	226.6 (6)[m]	0.70	22.1
Triethylamine	5.59 (2)		235.8 (2)[l]		1.18	28.8
Tri-*n*-propylamine	5.71 (2)		238.2 (2)[l]		1.30	31.2
Phosphine	4.70 (2)		187.9[n]		0.00	0.0
Methylphosphine	5.23 (2)		206.9[n]		0.53	19.0
Dimethylphosphine	5.55 (2)		218.9[n]		0.85	31.0
Trimethylphosphine	5.78 (2)		228.0[n]		1.08	40.1
Hydrogen sulfide	0.00		170 (3)[k]		0.00	0.0
Methanethiol	0.69 (3)		186[d]		0.69 (3)	16
Dimethyl sulfide	1.18 (3)		197[d]		1.18 (3)	27

[a] J. Long and B. Munson, *J. Am. Chem. Soc.*, **95**, 2427 (1973). [b] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969). [c] J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968). [d] J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971). [e] J. L. Beauchamp and R. C. Dunbar, *J. Am. Chem. Soc.*, **92**, 1477 (1970). [f] J. L. Beauchamp and M. C. Caserio, *ibid.*, **94**, 2638 (1972). [g] K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, **48**, 5205 (1968). [h] V. K. Potapov and V. V. Sorokin, *High Energy Chem. (Engl. Transl.)*, **4**, 508 (1970). [i] L. Hellner and L. W. Sieck, *J. Res. Natl. Bur. Stand., Sect. A*, **75**, 487 (1971). [j] J. Long, Ph.D. Thesis, University of Delaware, May 1972. [k] M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969). [l] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972). Note: ΔPA for NH_3 and CH_3NH_2 was estimated from a plot of IP vs. PA. [m] W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4728 (1972). [n] R. H. Staley and J. L. Beauchamp, *ibid.*, **96**, 6252 (1974).

ing two close peaks. This applies to the acids, but is worse for the esters because of the smaller separation in the ester peaks. The relative errors in both PA and E_B for the amines are quite small.

IV. Discussion

The relation of variations in proton affinity (PA), core-binding energy (E_B), and first (lone-pair) ionization poten-

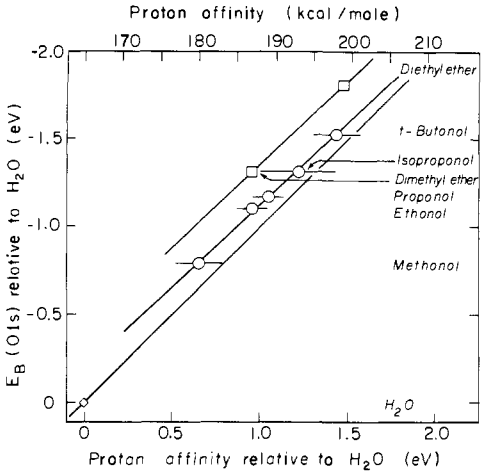


Figure 1. Oxygen 1s binding energies vs. proton affinities for single-bonded oxygens. Water is taken as the reference compound. Alcohols are denoted by circles and ethers by squares. The top two lines have slopes of 0.95, and the lowest line has unit slope. Errors in PA are shown; errors in E_B are smaller than symbols.

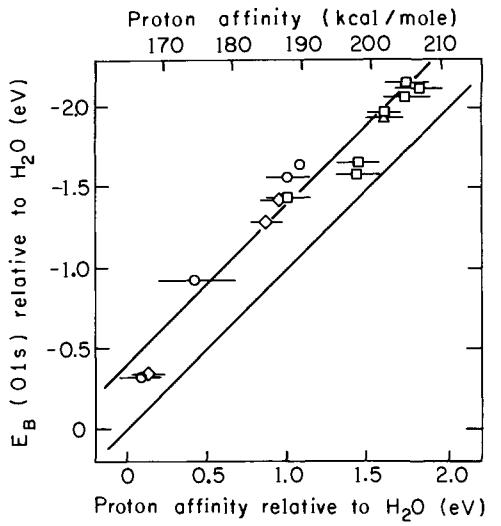


Figure 2. Oxygen 1s binding energies vs. proton affinities for double-bonded oxygen in acids (circles), esters (squares), aldehydes (diamonds), and acetone (triangle). The two lines of unit slope are offset by 0.4 eV. They pass through the data and the water reference point, respectively.

tial (IP) has been discussed previously.[4] Let us review this relationship briefly from two different points of view before discussing the data. First, the ionization potential corresponds to the reaction

$$B: \rightarrow B\cdot^+ + e^- \qquad IP \tag{2}$$

where, as in eq 1, the reaction energy is written on the right. Combining eq 1 and 2 with the binding energy of atomic hydrogen

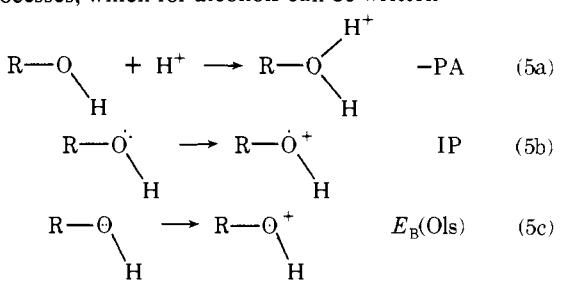
$$H \rightarrow H^+ + e^- \qquad e^2/2a_0 \tag{3}$$

we obtain

$$(B:H)^+ \rightarrow B\cdot^+ + H \qquad HA \tag{4}$$

If the hydrogen affinity HA is constant as the base B is changed, it follows that $\Delta PA = -\Delta IP$. This condition is surely not satisfied in general, but we may expect it to be satisfied within a homologous series. For a series of alcohols ROH, for example, HA should be only weakly dependent on R. As a first approximation this weak R dependence of HA might be absorbed as a constant in the ΔPA vs. $-\Delta IP$ relation. Thus PA and $-IP$ would vary together linearly, though not with unit slope. The core-level binding energy (E_B) can be incorporated into this linear variation if we note that E_B and IP should vary together (assuming that the lone pair is really an atomic pair), though not with unit slope.[10,11]

The second approach focuses on the similarity among the three processes, which for alcohols can be written



These equations were written to emphasize that in each case the ROH molecule is probed by a positive "test charge": the proton, the lone-pair hole, and the 1s hole, at the OH bond distance, the O2p radius, and the O1s radius, respectively. While the absolute magnitudes of PA, IP, and E_B are very different, their variation in each case depends largely on the R group's ability to stabilize the added localized positive charge by polarization. Thus as R is varied $-IP$, PA, and E_B should vary together linearly, though not with exactly unit slope (the slope should be approximately unity[4,5]). Because the "lone pair" can have some molecular orbital character, it is the least reliable test probe. As the R group becomes larger the linear variation should become more reliable, provided that the local environment of the active group is unchanged.

The data are discussed below in groupings that test various aspects of the correlations between E_B and PA.

A. Singly Bonded Oxygen. Figure 1 is a plot of E_B(O1s) vs. PA for those molecules in which oxygen is only singly bonded. The line of unit slope through the water point falls typically 0.1 eV below the alcohol points and 0.35 eV below the ether points. The latter data sets are each well fitted by lines of slope 0.95. It appears that substitution of an alkyl group for a hydrogen has a greater effect on E_B(O1s) than on PA, although uncertainties in the PA shifts, which for those compounds are much less accurately known than the E_B(O1s) shifts, leave a small residual doubt about this conclusion. The O1s binding energies for OH groups in acids and esters are not included in Figure 1 because the proton is believed to attach to the keto oxygen (see below). In fact these OH points would fall more than 1 eV below the lowest line in Figure 1.

B. Doubly Bonded Oxygen. The E_B(O1s) values are plotted against proton affinities in Figure 2, with the origin at the H_2O point. The acids and esters each showed two equally intense peaks in the O1s spectra, with separations ranging from 1.28 to 1.79 eV for the various molecules. It is natural to expect that the lower binding-energy peak belongs to the doubly bonded oxygen, on chemical grounds, because this oxygen is more negative. As pointed out by Carroll et al.,[6] theoretical estimates[12] of the O1s binding energies in formic acid support this assignment. In order to determine which peak corresponds to the carbonyl oxygen without invoking calculations or arguments about charge distribution, a spectrum of CH_3O-$COOCH_3$ (dimethyl carbonate) was obtained. This compound is very similar in structure to $CH_3(CH_2)$-$COOCH_3$ (methyl propionate) and gives a similar O1s spectrum except that the high-binding-energy peak is twice the area of the other. This must therefore be the ether oxygen, and the low-binding-energy peak arises from

the carbonyl oxygen. We are therefore confident that the O1s peaks are correctly assigned in these compounds.

Although the E_B(O1s) data do not by themselves give any indication of the protonation site in acids and esters, Carroll et al.[6] concluded from the E_B–PA correlation that protonation occurs at the keto oxygen, in disagreement with the assignment of Pesheck et al.[13] Our results agree with the assignment of Carroll et al. The "keto" oxygen correlation coincides with that of the aldehydes and ketones, while the "ether" oxygen correlation disagrees badly with the alcohol and ether values, as discussed above. Protonation apparently takes place at the keto oxygen.[14]

The range of E_B(O1s) values in the doubly bonded oxygen (Figure 2) is actually somewhat larger than in the singly bonded case (Figure 1). This occurs in spite of the fact that in the keto linkage the "active" oxygen atom is always shielded by a carbon atom from shifts arising from changes of substituents. We believe that the larger range of E_B(1s) values, and of proton affinities, in the doubly bonded oxygens arises because of an additive combination of inductive (initial-state) and polarization (final-state) effects. In the ether-linkage cases (Figure 1), by contrast, inductive shifts were relatively small because varying the alkyl groups did not change the oxygen charge very much.

The oxygen data can all be fitted reasonably well with the equation

$$\mathrm{PA} = \mathrm{PA}(H_2O) + 23.05[E_B(\mathrm{O1s},H_2O) - E_B(\mathrm{O1s},\mathrm{X})] - 7 \text{ kcal} \quad (6)$$

with proton affinities in kilocalories per mole and binding energies in electron volts. This equation should serve to predict proton affinities to ±5 kcal or better. Of course it applies only to those oxygens on which proton attachment occurs.

C. Nitrogen 1s Binding Energies in Amines. Aliphatic amines comprise another series for which gas-phase PA values are available. Indeed Aue et al.[15] have reported an accurate set of PA values with small relative errors, although their values for ammonia and methylamine were obtained by extrapolation of the PA–IP correlation. In Figure 3 we have plotted E_B(N1s) against the PA values. The E_B and PA scales are both relative, with ammonia taken as the reference compound. The absolute error in the PA of ammonia is shown in Figure 3.

In discussing the systematics of the E_B(N1s)–PA correlation, it is useful to divide the amines into primary, secondary, and tertiary groups, with methylamine, etc., comprising the first member of each group. We note first that a straight line of unit slope, curve A, fits roughly through all the data. All but four of the 16 compounds' points fall within 0.1 eV of curve A, and the worst deviation is 0.15 eV. Thus the relation

$$\Delta E_B = -\Delta\mathrm{PA} \quad (7)$$

is roughly confirmed.

The precision of the amine data permits a more detailed interpretation. Curve B, which is described by

$$\Delta E_B(\mathrm{N1s}) = -0.73\Delta\mathrm{PA} \quad (8)$$

passes through ammonia and its three methyl derivatives. Its slope shows that PA varies faster than E_B(N1s) when methyl is substituted for hydrogen. Within each amine series (primary, secondary, tertiary), however, the relation

$$\Delta E_B(\mathrm{N1s}) = -1.5\Delta\mathrm{PA} \quad (9)$$

fits the data quite accurately. This means that within a series a change of the substituent affects E_B(N1s) more than

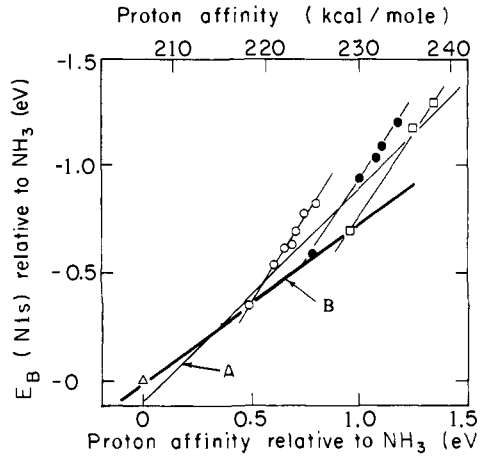


Figure 3. Nitrogen 1s binding energies vs. proton affinities for a series of aliphatic amines (Table I), using ammonia (triangle) as a reference. Primary amines are shown as open circles, secondary amines as filled circles, and tertiary amines as squares. Line A has slope unity and is drawn through all the data. Line B connects the ammonia, methylamine, dimethylamine, and trimethylamine points. The other lines show the linear variation within each series.

PA. The vertical IP within each series is also more sensitive to substituent change:[14]

$$\Delta\mathrm{IP} = -1.4\Delta\mathrm{PA}$$

The homolytic bond dissociation energy decreases upon substitution of larger alkyl groups. In fact we believe that all these observations can be interpreted in a self-consistent way that supports the earlier interpretations and yields additional insight into the proton addition reaction.

Two crucial points must be remembered. (1) The PA values are directly sensitive to details of local bonding at the nitrogen site, i.e., changes of angle, hybridization, etc. The vertical IP can be affected by hybridization and hyperconjugation but not angle changes. The E_B(N1s) parameter responds only to a change in the average potential, and may shift less. (2) If the local bonding at the nitrogen atom is kept constant, as in the series of primary amines for example, variations in the alkyl substituents will affect E_B, IP, and PA mainly through electron-electron shielding, either inductively (in the initial state) or through polarization in the final state. In either case the shift in E_B will exceed that in IP or PA.

The first point is consistent with the observation that in the group NH_3, methylamine, dimethylamine, trimethylamine, the three quantities E_B, IP, and PA vary linearly with one another but with slopes very different from unity. The total ranges are $\Delta E_B = -0.7$ eV, $\Delta\mathrm{IP} = 2.3$ eV, and $\Delta\mathrm{PA} = -1.0$ eV. The difference in sensitivities of IP on the one hand vs. E_B and PA on the other reflects the fact that the latter two quantities measure the molecule's response to a more localized test charge (a 1s hole or a proton), while the IP measures a much more complex property.

The second point can be interpreted more quantitatively. A distant perturbation (such as changing the length of an alkyl group) is felt locally at the nitrogen site through inductive or polarization effects. These are expressed as changes in the electron population in the valence shell of nitrogen in the initial and final states, respectively. In either case the N1s binding energy should vary as the two-electron Coulomb integral F^0(1s,2p) times Δn, the change in valence shell population, while for the IP this integral is replaced by F^0(2p,2p). This leads to larger shifts for inner shells, a well-known effect that has been discussed elsewhere.[10,11] We note that for a proton at the mean radius of the 2p shell in nitrogen the Coulombic interaction with N2p electrons

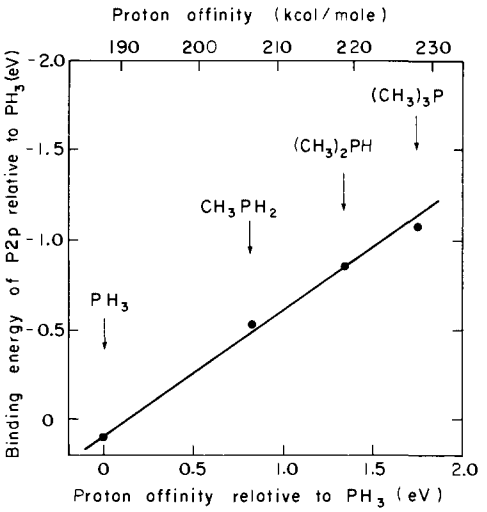


Figure 4. Phosphorus 2p binding energy plotted against proton affinity for phosphine and its methyl derivatives. The variation is linear, with a slope of −0.6.

would be of a similar magnitude but opposite sign compared to a 2p electron-electron interaction. Since, however, the proton is ~0.3 Å farther from the nucleus than the expectation value for the radius of a 2p electron, the shielding effect should be smaller. We therefore would predict

$$\frac{\Delta E_B(\mathrm{N1s})}{\Delta \mathrm{IP}} \simeq \frac{F^0(1s,2p)}{F^0(2p,2p)} = 1.45$$

$$\left|\frac{\Delta \mathrm{IP}}{\Delta \mathrm{PA}}\right| > 1$$

for the slope within a series of primary, etc., amines. The numerical ratio 1.45 was obtained by using Mann's integrals.[16] This is the ordering we see.

D. Shifts in Sulfur and Phosphorus. The E_B–PA comparison was extended to third-row elements by studying H_2S, phosphine, and their methyl derivatives. Sulfur and phosphorus differ from oxygen and nitrogen in having larger covalent radii, low-lying d orbitals, and lower electronegativity. Thus it was not clear what to expect. Only seven molecules were studied in this first attempt to extend the E_B–PA correlation to the third row, so only tentative conclusions can be drawn as yet. Thus far a surprisingly good correlation appears to exist.

Figure 4 shows a linear E_B(P2p)–PA correlation in the phosphorus compounds, but the slope is significantly less than one. This is interesting because the first IP follows the PA much more closely[17] (just the opposite from the amines). In other words, the homolytic bond dissociation is about constant. Nuclear rearrangement, or relaxation, in the protonated final state is important in the phosphines. This nuclear relaxation takes place upon protonation and with removal of a lone-pair electron (for the adiabatic IP) but not in the case of core ionization. It is possible to estimate the degree of angular rearrangement of the phosphines from the bond angles in the corresponding silanes, which are isoelectronic in the valence shells and have equal core charge. The H-P-H angle in phosphine is 93.3°, and the protonated ion is tetrahedral (109.5°). The corresponding angle change in trimethylphosphine is 98.9 to 110.2°. CNDO/2 calculations indicate that in the ground state the lone-pair orbital is mainly s-like, whereas in the protonated state the P-H bond is more nearly sp^3 in character. The steric strain moderation on substituting a less repulsive hydrogen for a lone pair is expected to be greater in the case of the methylated phosphines than in phosphine itself where the hydrogens are already over 2 Å apart in the initial state. Similar angle opening is expected upon ionization of one of the lone-pair electrons because a single electron is also less repulsive than a lone pair. Core ionization, however, should not cause significant angular relaxation. This might account for the poorer agreement between $-\Delta$PA and ΔE_B than between $-\Delta$PA and ΔIP. Of course there may be another reason for the observed behavior. Perhaps, for example, the fact that the ΔE_B–ΔPA correlation shows a low slope in the methyl derivatives of nitrogen and phosphorus (−0.7 and −0.6, respectively) is a clue that the same mechanism is operative in both cases.

In considering the sulfur compounds we first note that there are only three points and that the PA measurements were done by two different groups. It may, therefore, be fortuitous that $-\Delta\mathrm{PA} = \Delta E_B$ to within experimental error (Table I). Unfortunately for geometry change arguments of the type used above for the phosphines, we do not have the geometries for CH_3PH_2 or $(CH_3)_2PH$ which are isoelectronic with $CH_3SH_2^+$ and $(CH_3)_2SH^+$. If we assume, however, that the angles of the above phosphorus compounds are intermediate between those of PH_3 and $P(CH_3)_3$, the angles between the ligand bonds in CH_3SH and $(CH_3)_2S$ would decrease upon protonation. Comparison of SH_2 and PH_3 indicates that the H-S-H angle increases by only 1° upon protonation. While these arguments are not quantitative, it appears that relief of steric strain in the final protonated state is less important for the sulfur series.

V. Conclusions

The binding energy-proton affinity correlation has been extended by this work to 46 molecules, including molecules containing the third-row elements phosphorus and sulfur. The following conclusions were drawn. (1) The correlation holds up surprisingly well in the main, in both second- and third-row elements. (2) Extension to ethers (from H_2O and alcohols) and to larger alkyl amines shows that two correlations exist. All primary amines fall on one line, for example, while secondary amines are offset. This reflects the relative sensitivities of E_B and PA to long-range inductive effects vs. changes in local bonding. It may prove valuable in understanding variations in proton affinity. (3) Further evidence was obtained that protonation of carboxyl groups takes place at the keto oxygen. (4) The small slope of the correlation in phosphine derivatives and the unit slope in H_2S derivatives may be a consequence of nuclear relaxation, because the bond angles appear to change more in the former case.

The main conclusion to be drawn is that these additional results tie core-level binding-energy shifts firmly to a chemical property, the proton affinity. The proton and the core electron can be regarded as two "test charges" that probe both the static (initial-state) and dynamic (final-state) properties of a functional group. Used in a complementary way these two probes may yield insight into the electron dynamics of chemical reactions.

References and Notes

(1) J. N. Bronsted, *Recl. Trav. Chim. Pays-Bas*, **42**, 718 (1923).
(2) G. N. Lewis, "Valence", Dover Publications, New York, N.Y., 1966, p 142.
(3) J. I. Brauman and L. K. Blatt, *J. Am. Chem. Soc.*, **90**, 6562 (1968); J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971), and references cited therein.
(4) R. L. Martin and D. A. Shirley, *J. Am. Chem. Soc.*, **96**, 5299 (1974).
(5) D. W. Davis and W. Rabalais, *J. Am. Chem. Soc.*, **96**, 5305 (1974).
(6) T. X. Carroll, S. R. Smith, and T. D. Thomas, *J. Am. Chem. Soc.*, **97**, 659 (1975).
(7) W. L. Jolly, *Inorg. Synth.*, 11, 124 (1968).
(8) J. Long and B. Munson, *J. Am. Chem. Soc.*, **95**, 2427 (1973); L. Hellner and L. W. Sieck, *J. Res. Natl. Bur. Stand., Sec. A*, **75**, 487 (1971).
(9) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).
(10) D. A. Shirley, *Adv. Chem. Phys.*, **23**, 85 (1973).

(11) J. A. Hashmall, B. E. Mills, D. A. Shirley, and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **94**, 4445 (1972).
(12) D. W. Davis and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 173 (1974).
(13) C. V. Pesheck and S. E. Buttrill, Jr., *J. Am. Chem. Soc.*, **96**, 6027 (1974).
(14) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, in press.
(15) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **94**, 4726 (1972).
(16) J. B. Mann, "Atomic Structure Calculations I. Hartree Fock Energy Results for the Elements Hydrogen to Lawrencium", LA-3690, TID 4500.
(17) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 6252 (1974).

Nonbonded Attraction in Methyl Vinyl Ether

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Abstract: A detailed ab-initio investigation of the rotational surface of methyl vinyl ether shows that two stable isomers exist, the more "crowded" cisoid-staggered conformer being the structure of lowest energy. This conformational preference is in agreement with experimental results and can be understood in terms of a nonbonded attractive interactions between the methyl group and the double bond. Furthermore, the methyl rotational barriers in the cisoid and transoid conformations have been computed and their relative magnitudes can be also interpreted in terms of nonbonded interactions.

In our continuing studies of nonbonded interactions, we have investigated the conformational properties of the molecule methyl vinyl ether, $H_3COCH{=}CH_2$. This particular molecule was selected because it can serve as a prototype for the study of nonbonded attractive interactions and their influence upon molecular conformation. In this paper, the results of ab-initio calculations are reported and compared with experimental data. The computational results, in agreement with experimental evidence,[2] show that the most stable conformation of methyl vinyl ether is the one which a chemist might have dismissed on grounds of being "sterically" unfavorable. Subsequently, it is shown that this conformational preference can be understood in terms of a qualitative MO analysis based upon the ideas developed by one of the authors[3-5] and that these ideas are in full accord with the computational data.

Ab-Initio Calculations

In order to study the conformational properties of methyl vinyl ether two rotational motions have to be investigated (see Figure 1), i.e., rotation around the C_1–O bond (described here in terms of the torsional angle θ) and rotation around the O–C_2 bond (described in terms of the torsional angle Φ). The zero values of the two torsional angles correspond to the cisoid-eclipsed (CE) conformation. The computations were performed with the GAUSSIAN 70 series of programs[6] at two different levels of sophistication. We first made a detailed study of these two rotational motions with a STO-3G[7] basis set. These computations were carried out for various values of the angle Φ (Φ = 0, 45, 90, 120, 135, 155, and 180°) and at each Φ for various values of the angle θ (θ = 0, 30, 60, and 100°). At this computational level the following bond angles and bond lengths were kept constant (see Figure 1): $\angle HC_1H$ = 109.5°; $\angle HC_3H$ = 120°; $r(C_3\text{–}H)$ = $r(C_2\text{–}H)$ = 1.07 Å; and $r(C_1\text{–}H)$ = 1.09 Å. The remaining parameters were first optimized in the TE conformation, where important nonbonded interactions are absent, in the following order: (a) $\angle OC_2C_3$; (b) $\angle C_1OC_2$; (c) $r(C_2\text{–}C_3)$; (d) $r(C_2\text{–}O)$; (e) $\angle C_2C_3H$; and (f) $r(O\text{–}C_1)$. Furthermore, for the various conformations investigated, the following parameters were reoptimized: (i) $\angle OC_2C_3$ and $\angle C_2OC_1$ for all the conformations with θ = 0 and 60°; (ii) $\angle C_2OC_1$ for all the conformations with θ = 30 and 100° because $\angle OC_2C_3$ was found to have, in all cases, almost identical values at θ = 0 and 60° (in the computations at θ = 30° $\angle C_3C_2O$ was kept at the value obtained at θ = 0°, while for θ = 100° at the value obtained at θ = 60°); (iii) $r(C_2\text{–}O)$ for the conformations with θ = 0° (for all the conformations with the same Φ, $r(C_2\text{–}O)$ was kept fixed at the value obtained at θ = 0°).

In order to obtain more accurate estimates of the energy differences of interest, we carried out calculations for the conformations listed in Table I using a 4-31G basis set.[8] In the first stage we used the geometries optimized at the STO-3G level and these results are shown in Table I. In the second stage we reoptimized at the 4-31G level certain geometrical parameters which, on the basis of the STO-3G computations, appear to affect the energy the most, i.e., $r(O\text{–}C_2)$, $\angle OC_2C_3$, $\angle C_1OC_2$, and $\angle H_cC_1O$. The corresponding values, together with the total energies, are listed in Table II.

The potential energy curves for rotation about the O–C_2 bond, determined at the STO-3G and 4-31G levels, are shown in Figure 2. Here, we report only one curve at the 4-31G level, since the relative energies with and without geometry reoptimization are almost identical. The two curves at the STO-3G and 4-31G levels are very similar and predict that only two stable isomers exist: the CS (Φ = 0°) and TS (Φ = 180°) conformations. In both cases the planar CS conformer is the most stable isomer. The experimental studies[2] have suggested the existence of two rotamers of methyl vinyl ether with the more stable isomer having a planar cis conformation in accord with the ab initio result. However, there is some disagreement between the theoretical and experimental results about the structure of the less stable rotamer. Electron diffraction data[2c] suggest that it has a nonplanar heavy-atom skeleton with Φ in the range 80–110°, while the present computational results indicate a planar transoid form (Φ = 180°). It must be emphasized that this latter result has been obtained after a sophisticated geometry optimization. On the other hand, various assumptions were made in the least-squares refinement of the structural